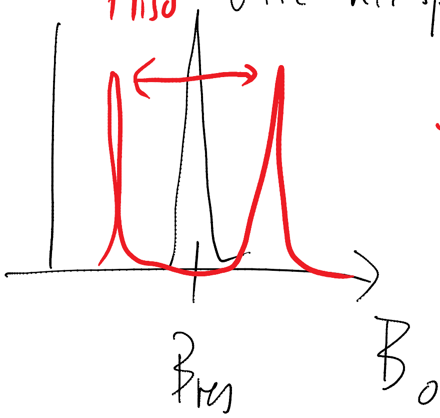
A_{iso} ohne Kernspin



$I = 1/2$

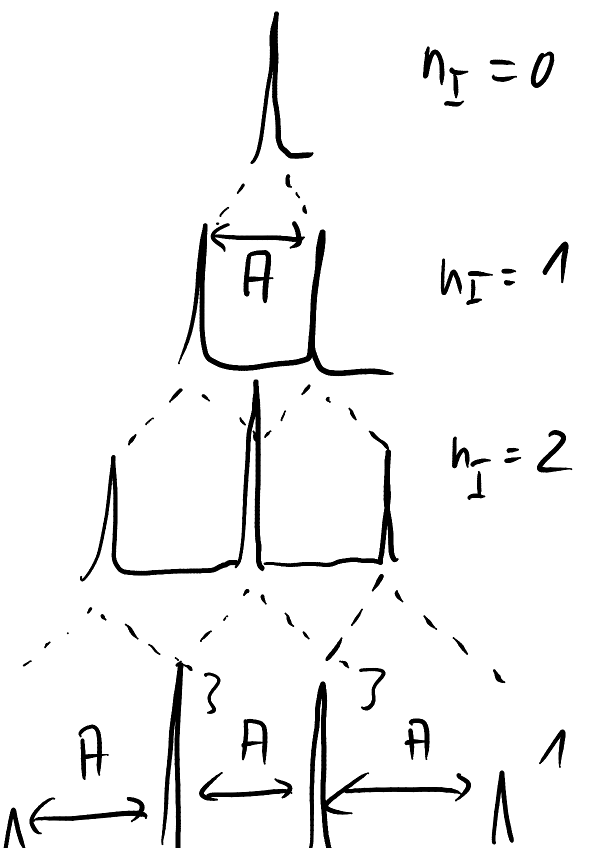
$$\omega_L = g_e \beta_e B_{res}$$

A_{iso} [G] isotrope hf-WW

$$\mu_0 = 4\pi \cdot 10^{-7} \frac{Vs}{Am}$$

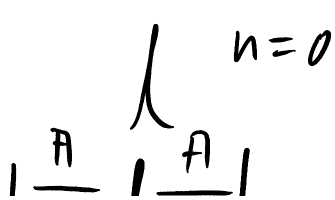
$$A_{iso} = \frac{2}{3} \mu_0 \cdot g_e \beta_e \cdot \gamma_I \left| \psi_e(I) \right|^2$$

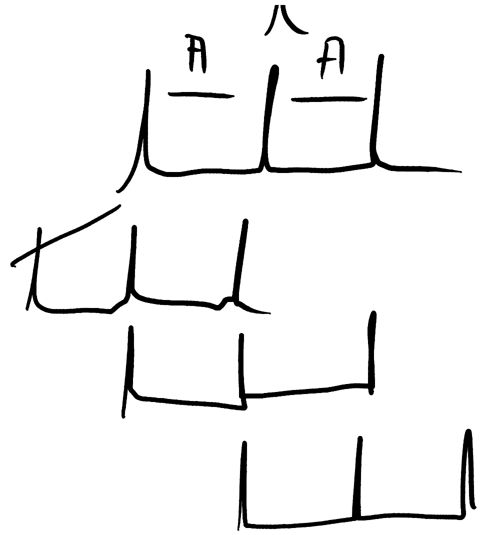
$CH_3^{\bullet}$



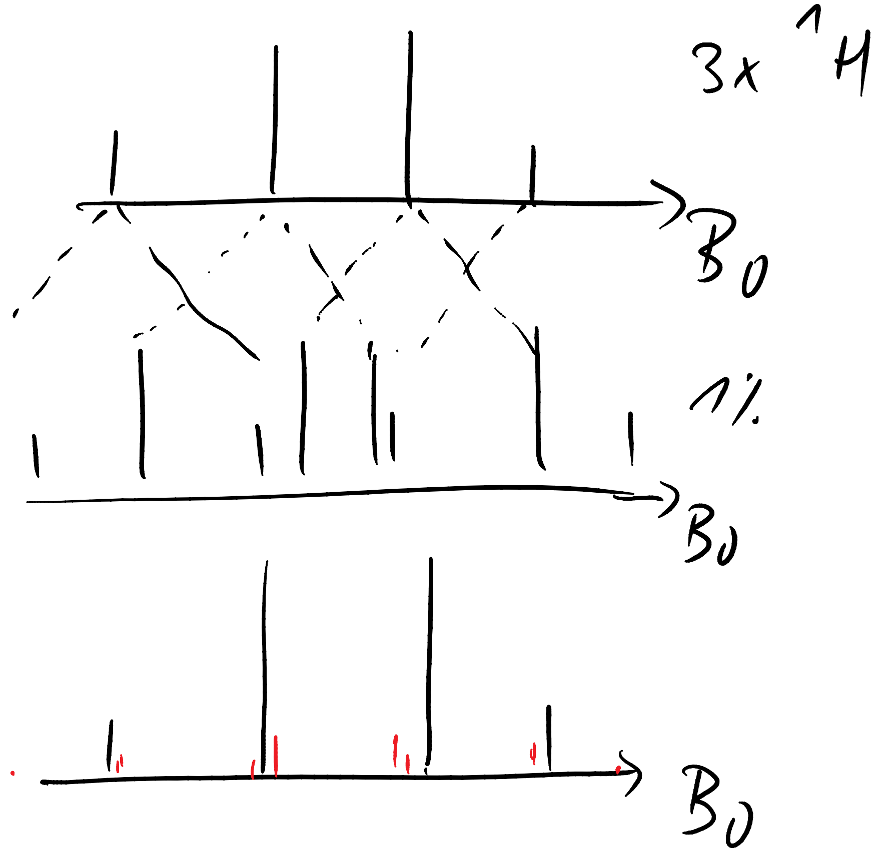
1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1 1
1 6 15 20 15 6 1

$I = 1$





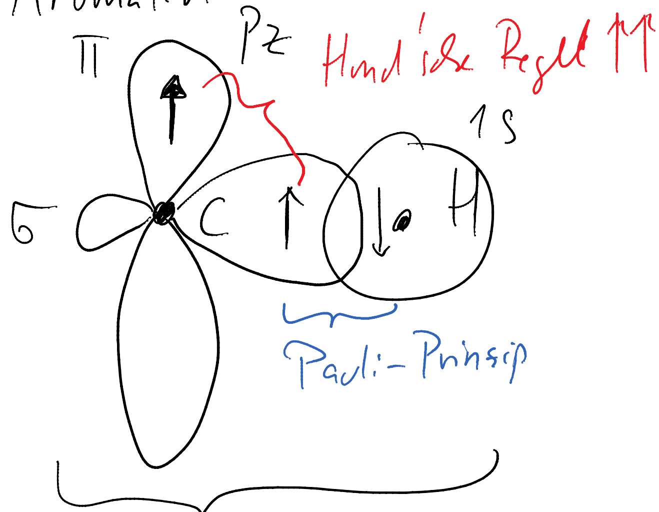
$CH_3^{\bullet}$

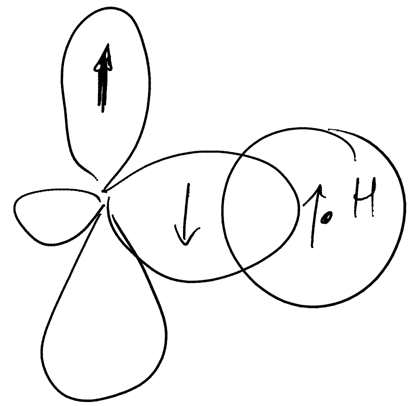


100% ^{13}C

1% ^{13}C

Aromaten





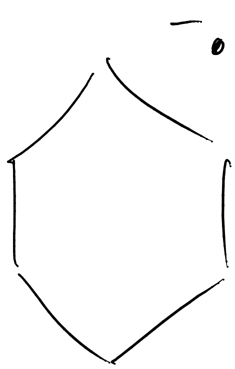
leicht bevorzugte Konfiguration

Indirekte HF-Kopplung über die C–H Bindungen

McConnell-Beziehung $a_H = Q \cdot \underbrace{\rho_\pi}$

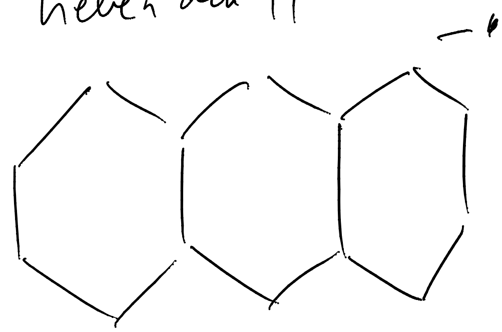
Spindichte des ungepaarten e^- im π-Orbital (pz) direkt neben dem H

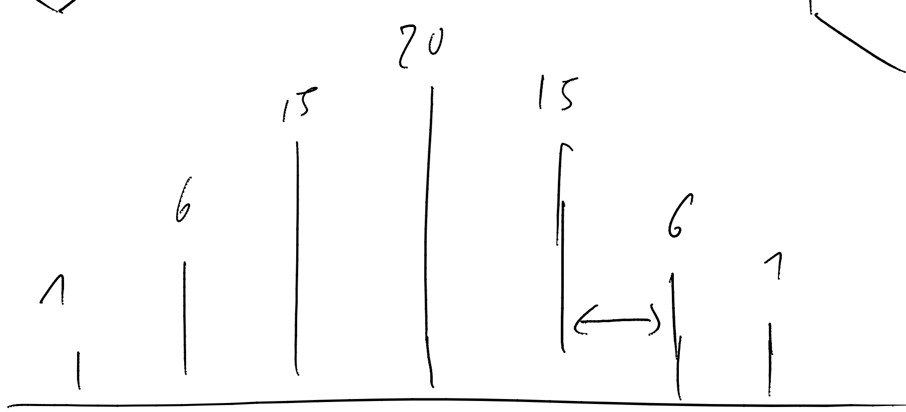
$\underline{Q = -22.5\ G}$



$\rho_\pi = 1/6$

$\underline{a_H} = -3.75\ G$





$$\mathcal{H}_S = g_e \beta_e \vec{B}_0 \vec{S}$$

$$\vec{B}_0 = (0, 0, B_0) \qquad \mathcal{H}_S = \underline{g_e} \beta_e B_0 \cdot \hat{S}_z$$

$$\hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$g_e = 2.0023 \ldots\ldots 14 \text{ Stellen}$$

$$\hat{\mathcal{H}}_S = \underbrace{\beta_e \vec{B}_0 \vec{L}}_{\text{Bahnmoment}} + \underbrace{g_e \beta_e \vec{B}_0 \vec{S}}_{\text{Spinmoment}}$$

$$\vec{B}_0 = (0, 0, B_0) \quad z\text{-Richtung}$$

$$\hat{\mathcal{H}}_S = \underbrace{\beta_e B_0 \hat{L}_z} + g_e \beta_e B_0 \hat{S}_z$$

$$\langle E \rangle = \beta_e B_0 \langle \Psi_0 | \hat{L}_z | \Psi_0 \rangle + g_e \beta_e B_0 \langle \alpha | S_z | \alpha \rangle$$

nur auf Bahn-wellenfkt. — nur Spin-Wellenfkt

$$\hat{L}_z = i\hbar \frac{\partial}{\partial \phi}$$

$L_z = -i\hbar \frac{\partial}{\partial\phi}$

$$\langle \hat{L}_z \rangle = i\hbar \int \psi_0^{\cancel{*}} \frac{\partial}{\partial\phi} \psi_0 \, dv = 0$$

falls ψ_0 reele Fktn $\leftarrow$ Grundzustand nicht entartet

$$\rightarrow \quad f \cdot g = \int f' g + \int g' f$$

$$\int \psi_0 \frac{\partial}{\partial\phi} \psi_0 \, dv = \frac{1}{2} \underbrace{\frac{\partial}{\partial\phi} \int \psi_0^2 \, dv}_{0}$$

Dienstag, 14. Mai 2013
16:43

Zahlenwerte für g_{iso} - Werte:

$$g_e = 2.002322$$

Molekül	g-Wert
Benzosemichinon$^{-\bullet}$	2.004665
Naphtalen$^{-\bullet}$	2.002743
DPPH	2.0037
Tyrosyl^{-}	2.0053
Chlorophyll-Dimer$^{+\bullet}$	2.00270

Δg sind klein

Spin-Bahn-Kopplung ist Ursache für Abweichung vom freien e^- g-Faktor

Dienstag, 14. Mai 2013
16:47

Spin-Bahn Kopplungsterm $\mathcal{H}_{SB} = \xi \vec{L} \cdot \vec{S}$

$$\hat{\vec{L}} \cdot \hat{\vec{S}} = \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z$$

$$= \underbrace{\frac{1}{2}\left(L^+ S^- + L^- S^+\right)}_{\text{Mischung von den Spinzuständen } |\alpha\rangle, |\beta\rangle} + \hat{L}_z \cdot \hat{S}_z$$

$$L^+ = L_x + i L_y$$

$$L^- = L_x - i L_y$$

$$\hat{\mathcal{H}} = \beta_e B_0 \left(g_{zx} \hat{S}_x + g_{zy} \hat{S}_y + g_{zz} \hat{S}_z \right)$$

$$= \frac{1}{2} \beta_e B_0 \begin{bmatrix} g_{zz} & g_{zx} - i g_{zy} \\ g_{zx} + i g_{zy} & -g_{zz} \end{bmatrix}$$

$$g_{zz} = g_e - 2\xi \sum_n \frac{\langle \psi_0 | L_z | \psi_n \rangle \langle \psi_n | L_z | \psi_0 \rangle}{E_n - E_0}$$

$$g_{zx} = g_e - 2\xi \sum_n \frac{\langle \psi_0 | L_z | \psi_n \rangle \langle \psi_n | L_x | \psi_0 \rangle}{E_n - E_0}$$

Beispiel: ^1H

$2s$ —— $2p$ —— $\ell = 1$

ψ_1 $2p_x\ 2p_y$ $m_\ell = \pm 1$

$\updownarrow \Delta E$

ψ_0 $2p_z$ $m_\ell = 0$

$4.5 \cdot 10^{-5}\,eV$ $\vec{S}\vec{L}$ WW

$1s$ ——

$p_0 = \psi_0 = p_z$ $\qquad |\alpha\rangle, |\beta\rangle$

$p_{+1} = -\frac{1}{\sqrt{2}}(p_x + ip_y)$

$p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$

$$\langle m_\ell+1|L^+|m_\ell\rangle = \langle m_\ell|L^-|m_\ell+1\rangle = \sqrt{\ell(\ell+1) - m_\ell(m_\ell+1)}$$

$L^+|p_0\rangle = \sqrt{2}\cdot|p_{+1}\rangle \qquad L_z|p_0\rangle = 0\cdot|p_0\rangle$

$L^-|p_0\rangle = \sqrt{2}\cdot|p_{-1}\rangle$

$$g_{zz} = g_e - 2\cdot\xi \sum_{n=1}^{2} \frac{\langle\psi_0|L_z|\psi_n\rangle\langle\psi_n|L_z|\psi_0\rangle}{\Delta E}$$

$$= g_e - 2\xi\left\{\frac{\langle\psi_0|L_z|\psi_1\rangle\langle\psi_1|\overset{0}{\cancel{L_z|\psi_0}}\rangle}{\Delta E} + \frac{\langle\psi_0|L_z|\psi_{-1}\rangle\langle\overset{0}{\cancel{\psi_{-1}|L_z|\psi_0}}\rangle}{\Delta E}\right\}$$

$$= g_e \text{ (unverändert)}$$

$$g_{xx} = g_e - 2\xi\left\{\frac{\langle p_0|L_x|p_{+1}\rangle\langle p_{+1}|L_x|p_0\rangle}{\Delta E} + \frac{\langle p_0|L_x|p_{-1}\rangle\langle p_{-1}|L_x|p_0\rangle}{\Delta E}\right\}$$

$$\left.\begin{aligned} L^+ &= L_x + iL_y \\ L^- &= L_x - iL_y \end{aligned}\right\} \quad L^+ + L^- = 2L_x$$

$$g_{xx} = g_e - \frac{\xi}{2}\left\{\frac{\langle p_0|L^+ - L^-|p_{+1}\rangle\langle p_{+1}|L^+ + L^-|p_0\rangle}{\Delta E} + \frac{\langle p_0|L^+ + L^-|p_{-1}\rangle\langle p_{-1}|L^+ + L^-|p_0\rangle}{\Delta E}\right\}$$

alle anderen Terme $= 0$

$$= g_e - \frac{\xi}{2}\left\{ \frac{\langle p_0 | L^- | p_{+1}\rangle \langle p_{+1} | L^+ | p_0\rangle}{\Delta E} + \frac{\langle p_0 | L^+ | p_{-1}\rangle \langle p_{-1} | L^- | p_0\rangle}{\Delta E} \right\}$$

$$= g_e - \frac{\xi}{2}\left\{ \frac{2}{\Delta E} + \frac{2}{\Delta E} \right\} = g_e - \frac{2\xi}{\Delta E}$$ genauso g_{yy}

$$g_{iso} = \frac{1}{3}\left(g_{xx} + g_{yy} + g_{zz}\right) = g_e - \frac{4}{3}\frac{\xi}{\Delta E}$$

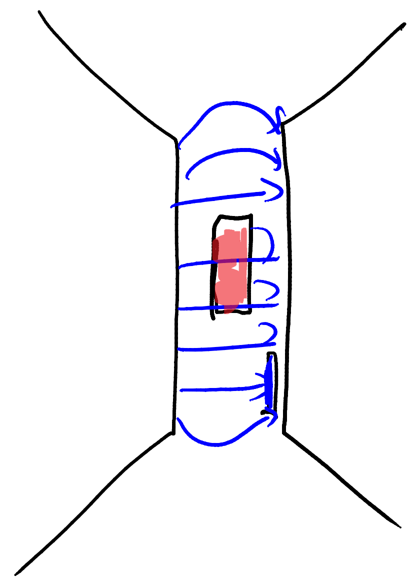
Spin-Bahn-Kopplungsparameter für p-Zustände:

B	$11\ cm^{-1}$	F	$270\ cm^{-1}$
C	$28\ cm^{-1}$	Br	$2460\ cm^{-1}$

Experimentelle Bestimmung von Radikal-g-Faktor:

$$\nu_{MW}^{Res} = g_s \cdot \beta_e \cdot B_0$$

Bestimmung der MW-Frequenz leicht auf 1 kHz möglich



Messung mit Eichsubstanz

g_{mess} $g_{Referenz}$

$$\frac{g_{mess}}{g_{Referenz}} = f$$